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## PROTECTION AND RETENTION OF THE QUALITY OF FLOAT GLASS SURFACE

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A method for active protection of the float glass surface from leaching based on spraying an aqueous phosphate solution on the surface of the moving glass band in the temperature interval of 120–560°C is considered. The coating provides for additional chemical modification of the glass surface and extends its storage period.

The main factor which impairs the quality of the float glass surface in long-term storage and service is water. Water resistance of sheet glass is the quantitative criterion for assessing the quality of the glass surface.

An increase in water resistance of glass through optimization of the technological parameters (chemical composition, hydrogen content in the melt tank, and the glass melt temperature in the through channel) is only possible at the initial stage of leaching in the first 6 h of the moisture effect [1]. In long-term testing of glass water resistance, the tendency for a decrease in the water resistance of the glass surface is quite perceptible.

One of the disadvantages of the float process consists in the fact that the properties of sheet glass produced by the float method, in particular, its mechanical strength and chemical stability, change with time. The formation of the glass band at the exit from the melt tank is not completed. The glass surface is saturated with noncompensated bonds and at the exit from the melt tank starts actively reacting with the gases of the ambient atmosphere of the workshop.

As the process of atmospheric damage to the glass surface evolves, the glass quality and strength parameters deteriorate.

According to the results of a number of papers, a significant increase in water resistance of glass can be accomplished only by using modifying protective coatings (patents USA 3577256, France 1514571) [2]. Of particular interest is the method for molding glass sheets with modified surfaces.

Our purpose consisted in selecting specific reactants for treatment of the freshly molded float glass surface which would allow for simultaneous modification of the surface layer structure and formation of a protective coating against the undesirable effect of a moist atmosphere.

Analysis of published and experimental data indicated that promising reactants that can be used as protective coatings are high-molecular phosphates.

The initial material for the production of protective modifying phosphate coatings were salts of phosphoric acid. They were ammonium hydrophosphate  $\text{NH}_4\text{H}_2\text{PO}_4$  with impurities of water-soluble  $(\text{NH}_4)\text{HPO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  and water-insoluble phosphates  $\text{CaHPO}_4$ ,  $\text{MgNH}_4\text{PO}_4$ , and aluminioammonium-ferrous phosphates.

To deposit a coating, a 5% solution of phosphate salts in distilled water was prepared and filtered by decantation to separate the water-insoluble components. The resulting solution was sprayed on the hot freshly-molded upper surface of the glass band in different temperature zones of the annealing furnace and at the exit from the furnace.

An experimental device was designed for the treatment of the glass band with aqueous phosphate solution, which is schematically shown in Fig. 1. The device includes the following units: titanium injectors with adjustable solution feed; a pipeline system for supplying the liquid reactant and compressed air, a container to hold the solution, equipped with a level gauge.

The industrial experiments were performed on the EPKS-4000 line within the temperature range of 200–525°C. As a consequence, in addition to the formation of protective coating, the glass surface underwent thermochemical modification due to the leaching of its surface in the course of diffusion ionic exchange of sodium with the surface components.

Depending on the temperature of the glass band in the site of the solution spraying, the resulting coating was either a semitransparent solid film with disruptions of continuity manifested by pores (at 350–525°C), or a transparent wax-like film in the form of a viscous continuous layer (at 200–250°C).

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The trial glass sheets produced in the course of the experiments were for a long period stacked in four pyramids in the same workshop where the reference glass manufactured at the same time was stored as well. The tested glass consisted of sheets  $1200 \times 1600 \times 5$  mm.

Samples of the reference glass and the experimental glass were tested for their physicomachanical properties: water resistance, microhardness, mechanical strength, light transmission, and chemical composition of the glass surface layer.

Studies of the chemical composition of the surface layer performed by x-ray microscopic analysis after the removal of the protective phosphate coating revealed that with increasing temperature of deposition of the coating, the glass surface becomes saturated with phosphoric oxide and depleted of sodium oxide (Table 1). This is a direct indication of the modifying nature of the coating.

It is seen in Table 1 that as the temperature of the deposition of the phosphate coating decreases, its light transmission increases, and with a deposition temperature of  $250^\circ\text{C}$ , the light transmission of the coating is virtually the same as the light transmission of the glass itself.

Table 2 shows the parameters of thermally polished glass after the removal of the modifying coating registered immediately after molding and after two years of storage in stacks.

The measurements performed by the standard methods indicated that the strength properties of the glass are improved, especially the surface water resistance. At the same time, the water resistance of the modified surface significantly increases after long-term storage of the glass. Apparently, the leaching of the glass surface persists in the course

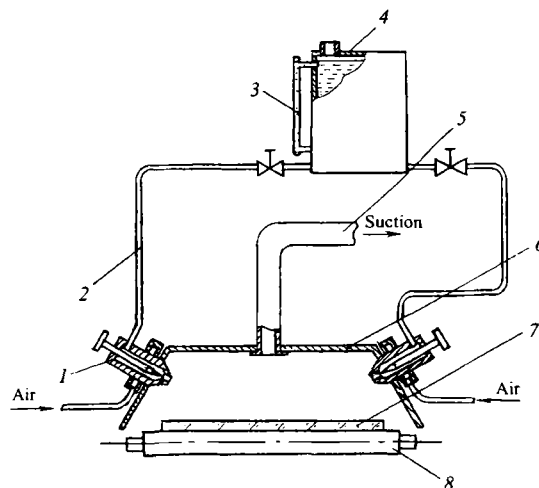


Fig. 1. Experimental device for deposition of phosphate solution: 1) injector; 2) pipeline; 3) level gauge; 4) container; 5) suction; 6) casing; 7) glass; 8) shaft.

of its storage due to the diffusion ionic exchange of sodium and the coating components.

However, when glass with a phosphate coating is manufactured in industrial conditions, part of the glass with the phosphate film is inevitably returned to the furnace in the form of cullet. Consequently, we are faced with the problem of the effect of the phosphates introduced as part of recycled cullet on the chemical composition and crystallizing capability of the glass.

Let us consider the extreme variant when 100% cullet with the phosphate film gets into the furnace. The maximum

TABLE 1

Temperature of coating deposition, $^\circ\text{C}$	Chemical composition of surface glass layer, wt. %						Optical transmission of coating, %
	$\text{Na}_2\text{O}$	$\text{MgO}$	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{CaO}$	$\text{P}_2\text{O}_5$	
525	12.13	3.37	1.48	74.62	8.00	0.34	43
470	12.51	3.40	1.34	74.08	8.09	0.23	52
350	13.05	3.51	1.29	73.44	8.12	0.19	66
250	13.37	3.48	1.42	72.86	8.04	0.14	74
Without coating	15.44	3.21	1.48	71.68	7.79	0.00	75

TABLE 2

Parameter	Temperature of coating deposition, °C								Without treatment	
	525		470		350		250		Freshly molded surface	After 2 years of storage
	Freshly molded surface	After 2 years of storage	Freshly molded surface	After 2 years of storage	Freshly molded surface	After 2 years of storage	Freshly molded surface	After 2 years of storage		
Average strength, MPa	305	314	268	312	245	252	220	250	124	112
Microhardness, GPa	5.60	5.48	6.10	5.88	5.50	5.47	5.30	5.20	5.20	5.11
Water resistance (Na <sub>2</sub> O leaching), mg/dm <sup>2</sup>	0.042	0.040	0.061	0.040	0.068	0.038	0.068	0.031	0.110	0.110

content of phosphoric anhydride in the glass melt in this case would be 0.00033%.

Phosphates at the temperature of glass melting are volatile components. It is known that the volatility of phosphoric anhydride in opacified glass melting is about 7.5 wt.%. [3]. Hence, the amount of phosphoric anhydride remaining in the glass-melting furnace does not exceed 0.0003%.

Investigations headed by B. G. Varshal revealed that an additive of up to 0.4%  $P_2O_5$  to the glass composition does not produce significant alteration in the glass melt properties (viscosity, density, etc.), whereas at the same time, the homogeneity of the glass improves and its propensity to crystallization decreases [4].

Moreover, the use of phosphates as a protective coating is environmentally safe since salts of phosphoric acid have low toxicity. The phosphoric acid anion is "physiological," i.e., it is part of human blood composition, and therefore, its salts can produce an overall toxic effect only in extremely high quantities.

That is why phosphoritis may occur in personnel employed in mining and processing of phosphorites, apatites, and similar large-capacity production processes. The maxi-

mum admissible phosphate concentration in air for these processes is  $6 \text{ mg/m}^3$ . Our technology involves the use of aqueous solutions of phosphates, whereas the consumption of dry phosphate material is  $0.078 \text{ mg per } 1 \text{ m}^2$ .

Thus, the proposed technology of producing float glass with a surface resistant to the ambient environment effects makes it possible to extend the storage term of this glass to 1 year and more and, consequently, to improve the sheet glass quality.

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